

UTILIZATION CHITOSAN-*p-t*-BUTYLCALIX[4]ARENE FOR RED MX 8B ADSORBENT

D S HANDAYANI, T KUSUMANINGSIH, L A HAK

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University

E-mail: dsuci72@gmail.com

Abstract. Adsorption of *Procion Red MX 8B* using chitosan dan chitosan-linked *p-t*-butylcalix[4]arene has been done. The research aimed to understand the adsorption of *Procion Red MX 8B* using chitosan *p-t*-butylcalix[4]arene compared to ordinary chitosan. The research was conducted in a batch process varying in pH, contact time and initial concentration of the *Procion Red MX 8B*. The amount of dye adsorbed was determined using UV-Vis spectrophotometer and the adsorbent was characterized using FTIR and SEM-EDX spectrophotometer. The result showed that the optimum condition was achieved when the pH was set at 4, contact time 135 minutes and initial concentration at 200 ppm. The kinetic analysis showed that the adsorption followed Ho kinetic model and pseudo second order with the adsorption rate constant was 3.69×10^{-3} g/mg.minute and 2.03×10^{-3} g/mg.minute. The isotherm analysis showed that the adsorption process tend to occur following the Langmuir model with maximum capacity for chitosan and chitosan-linked *p-t*-butylcalix[4]arene 136.09 mg/g and 147.35 mg/g respectively. The adsorption energy of chitosan and chitosan-linked *p-t*-butylcalix[4]arene at 30.53 kJ/mole and 33.65 kJ/mole.

1. Introduction

The development of industrialization, besides bringing benefits also cause environmental problems, namely the emergence of environmental pollution and destruction of one of them is the emission of pollutants into the environment. Industrial liquid waste is a pollutant that causes negative environmental impact. The liquid waste containing hazardous materials and toxic contained in the water, can block the sun shone through the aquatic environment, thereby disrupting the biological processes [1].

One of the industry, namely the liquid waste of batik industry in the form of waste dye. Waste water of Batik industrial was originating from the dyeing, washing, printing and finishing proses. Waste dyed of batik industry contains several components of which the rest of the dye, salt and additive materials such as urea, sodium alginate, sodium bicarbonate and water residual staining and washing. Reactive dyes are often used in the batik industry include Procion, Cibracon, Drimaren, Lavafix, Remazol, forecasts allowing, and Primazin [2].

Many methods have been developed for waste treatment dye in the waters that coagulation, adsorption [3] and ion exchange [4]. Coagulation method will produce sludge in relatively large amounts. The resulting sludge was eventually going to create new problems for waste processing unit [5], ion exchange

method and reverse osmosis are generally effective, but requires equipment and operating costs are relatively high. Effective method used to treat waste is the adsorption of the dye, because the excess of adsorption methods, among others, the process is relatively simple, relatively high effectiveness and efficiency, and do not give side effects such toxic substances [6]. Additionally adsorption method is one method that can work at low concentrations, can be recycled, and costs are relatively cheap [7].

Several studies of wastewater treatment dye adsorption proved to effectively reduce the concentration of the dye in the water. The adsorbent used comes from synthetic and natural. Synthetic adsorbent has been used, among others PSF-EGDE-CTS (polisulfon-ethylene glycol diglycidyl ether-chitosan) [8] to adsorb Procion Red MX 8B dye in textile waste batik and clay pillared CTMA-Al (cetiltrimetil ammonium-aluminium) [9] to adsorb dye indigo karmina. The adsorbent of nature, among others Aryunani [3] have investigated the the adsorption of the dye textile Remazol Yellow on the batik waste using water hyacinth activated NaOH. Setyoningsih [1] was using a pineapple leaf fibers to adsorb dye Procion Red MX 8B. The use of natural adsorbent that is cheap and plentiful in nature certainly is expected by the researchers, but to find the active compound can be used as an effective adsorbent is not easy, it can be difficult to explain the adsorption phenomena occurring in the adsorbent used. It is therefore necessary to find another adsorbent the structure, chemical and physical properties are known with certainty, and this can be obtained from the results of previous studies. Terms absorbent good, among others, have absorption large, is a solid that has a large surface area, should not be soluble in the substance to be adsorbed, must not engage in a chemical reaction with the mixture to be purified, can be regenerated back easily and non-toxic [10].

Chitosan is adsorbent with structure, chemical and physical properties are already known with certainty. It is abundant in nature and a good adsorbent criteria. Chitosan is the result of deacetylation of chitin which has undergone the removal of acetyl groups. Acetyl group is missing from the process, leaving deacetylation free amino group that causes the chitosan to be polycationic [11]. Research on the application of chitosan as an adsorbent has been done by some researchers that once used to adsorption of Procion Red MX 8B dye include Kusumaningsih et al [8] and Astuti [12], but has adsorption capability and low adsorption capacity (19.02 mg/g and 12.52 mg/g). Chitosan had specific properties such as biocompatibility, non-toxic and renewable makes a biopolymer chitosan serious attention to continue to be developed and researched. Improving the ability of chitosan can be fastened on a cross-linked macromolecular compounds crown ether is p-t-butylcalix[4]arene. The compound of p-t-butylcalix[4]arene has a geometry such as baskets and hollow, can be used in guest-host systems [13]. Modifications to improve the ability of chitosan as an adsorbent that is by p-t-butylcalix[4]arene attached to the chitosan has been done by Hilmiyana [14] who successfully apply to Procion Red MX 8B dye.

This research has been conducted on dye adsorption others, namely Procion Red MX 8B dye using butylcalix[4]arene tied to the chitosan results of research Handayani [15]. The Procion Red MX 8B dye is a reactive dye dichlorotriazine group that can undergo substitution reaction with the fibers and form ester bond that has the highest reactivity compared to other classes of dyes [8]. Waste of Procion Red MX 8B dye off for having reported carcinogenic azo group [16]. Therefore, the chitosan-p-t-butylcalix[4]arene expected to be effective and efficient way to reduce environmental pollution, especially in the batik industry.

2. Experimental

2.1. Ingredients:

Chitosan, Chitosan-p-t-butylcalix[4]arene (synthesized by Handayani [15]), NaOH Merck., HNO₃ Merck, *Procion Red MX 8B* dye

2.2. Instruments:

Stirrer Adsorption (CV INTAN Yogyakarta), Fourier Transform Infra Red (FTIR) Prestige-21 Shimadzu, Scanning Electron Microscopy (SEM) JEOL JSM 6360 - EDX (JED-2200 and UV-Vis Spectroscopy Optima SP-300

2.3. Procedure:

2.3.1. Effect of solution pH Procion Red MX 8B

A total of 25 mL of Procion Red MX 8B at a concentration of 100 ppm respectively set the initial pH to 1.5; 2; 4; 6; 8; 10 with HNO₃ and NaOH. Then into each solution was added 20 mg of chitosan-p-t-butylcalix[4]arene. The mixture was stirred at a speed of 200 rpm for 2 hours. Afterwards the solution was filtered and the filtrate was analyzed by UV-Vis spectroscopy. Equal treatment performed on chitosan as a comparison.

2.3.2. Effect of Stirring Time

A total of 25 mL of Procion Red MX 8B each with a variation of time at 5, 15, 45, 135, 405 minutes was set at optimum pH. Then into a solution, 20 mg of chitosan-p-t-butylcalix[4]arenes adsorbent was added and stirred for optimum time with a speed of 200 rpm. The solution is then filtered and analyzed by UV-Vis spectroscopy. Equal treatment performed on chitosan as a comparison.

2.3.3. Influence of Solution Concentration Procion Red MX 8B

A total of 25 mL of Procion Red MX 8B each with varying concentrations of 100, 150, 200, 250, 300 ppm was set at optimum pH. Then into a solution, 20 mg of chitosan-p-t-butylcalix[4]arenes adsorbent was added and stirred for optimum time with a speed of 200 rpm. The solution is then filtered and analyzed by UV-Vis spectroscopy. The same treatment was done for chitosan as a comparison.

3. Results And Discussion

3.1. Determination of Optimum pH

The adsorption process depends on the type of adsorbent, the adsorbed species and the type of solvent. PH variation on the research done at the initial pH solution of pH 1.5; 2; 4; 6; 8; 10; 11 and 12. Figure 1 showed the curve of the adsorption of the dye Procion Red MX 8B by chitosan and chitosan-p-t-butylcalix[4]arenes at various pH. Figure 1 can be seen that the adsorption occurs at a pH of acids and bases with the highest absorption capacity exist at pH 4, so that the optimum pH is pH 4 to chitosan and chitosan-p-t-butylcalix[4]arenes with the adsorption capacity of 82.94 and 99.74 mg/g. The solution to the acid conditions of the hydrogen atoms (H⁺) can occur protonated amine group (-NH₂) of chitosan. In aqueous solution, the dye will dissolve and sulfonate groups to the reactive dye Procion Red MX 8B occurs dissociation and transformed into ions.

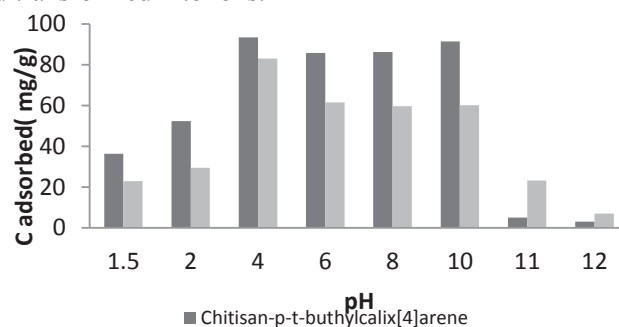


Figure 1. Concentration of dye absorbed Procion Red MX 8B on the variation of pH

When the acidic conditions, the hydrogen bonds also contribute to the the adsorption process. Hydrogen bonding occurs between nitrogen from chloride sianurate dye with hydrogen from the OH groups of chitosan [12]. When an alkaline condition, the adsorption by chitosan can still occur. This is in accordance with the opinion of Sakkayawong et al. [17].

The adsorption process at alkaline pH can be explained by the presence of ions (CH_2O^-) of chitosan covalently bound to the dye replace the cluster chloride (Cl) are separated into solution. Therefore pH 8 to pH 10 increased adsorption power but not as high at pH 4 and pH down again at 11 and 12. The decrease adsorption occurs in alkaline conditions due to the hydroxyl group (OH) of the water molecules react perfectly with the dye , thus causing the interaction between the dye with an adsorbent decreases.

The adsorption capacity of chitosan-p-t-butylcalix[4]arenes at pH 4 in the amount of 93.35 mg/g. The results presented almost the same as the adsorption by chitosan, but the adsorption by chitosan-p-t-butylcalix[4]arenes showed better adsorption of the chitosan. In acidic conditions, reactive groups chitosan-p-t-butylcalix[4]arenes that has been protonated more stable and form molecules of chitosan-p-t-butylcalix[4]arenes itself shaped basket and hollow thus indicated that the dye Procion Red MX 8B trapped so that the maximum adsorption. A process of return electrostatic interaction between the amine group with sulfonate groups of dye, like chitosan, but the chitosan-p-t-butylcalix[4]arenes such as secondary amines. The process that occurs on the same basic conditions such as adsorption by chitosan, in which the hydroxyl groups of chitosan-p-t-butylcalix[4]arenes attack chloride groups of the dye and binds covalently to the dye. But in the presence of water molecules, allowing competition between the hydroxyl group (OH) of the water molecules and hydroxyl groups of the chitosan-p-t-butylcalix[4]arenes to bind with the dye as the reaction expressed by Christie [18].

3.2. Effect of Contact Time and Parameter Kinetics

Contact time was the time required adsorbent to adsorb Procion Red MX 8B dye. The time variation contacts made in this study was 5; 15; 45; 135 and 405 minutes. Effect of contact time on the amount of adsorbed dye can be seen in Figure 2.

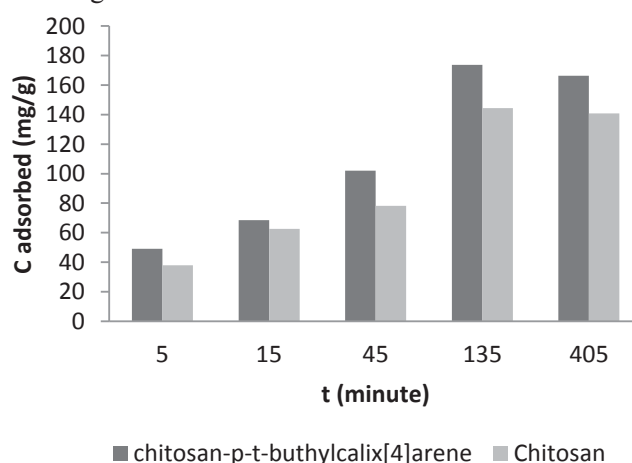


Figure 2. Concentration of dye Procion Red MX 8B on the variation of contact time

The optimum contact time for both the adsorbent was reached at minute 135. The concentration of the dye Procion Red MX 8B absorbed as much as 144.34 mg/g of chitosan and 173.79 mg/g for the chitosan-p-t-butylcalix[4]arenes. Results of the adsorption kinetics study in the two adsorbents shown in Table 1.

Table 1. Assessment of the dye adsorption kinetics Procion Red MX 8B

adsorption kinetics	Adsorbent	
	Chitosan	chitosan-p-t-butylcalix[4]arene
Lagergren:		
– K (min ⁻¹)	0.015	0,017
– R ²	0.804	0,896
Ho:		
– K (g mg ⁻¹ min ⁻¹)	3.69 x 10 ⁻³	2.03 x 10 ⁻³
– R ²	0.983	0.963

3.3. Effect of Initial Concentration Dyes and Parameter Isotherm

Adsorption capacity Procion Red MX 8B of the adsorbent chitosan and chitosan-p-t-butylcalix[4]arene carried out under optimum pH and time that has been obtained previously. Effect of initial concentration of dye Procion Red MX 8B of the adsorbent defined in Figure 3.

Figure 5 showed the adsorption concentration tended to increase with increasing concentration of adsorbate and then remained relatively constant at a concentration of 200 ppm for both types of adsorbents. Study of adsorption isotherms determined whether the dye adsorption with adsorbent followed the Langmuir isotherm or Freundlich isotherm.

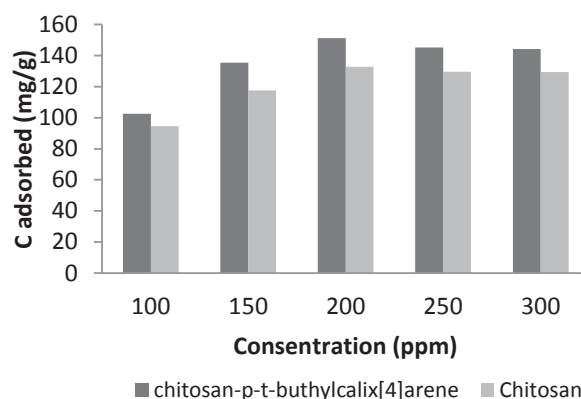


Figure 3. Variation of Initial concentration dyes Procion Red MX 8B

The study results dye adsorption isotherm Procion Red MX 8B using adsorbents chitosan and chitosan-p-t-butylcalix[4]arene are presented in Table 2.

Table 2. Parameters of isotherm adsorption of Procion Red MX 8B

Adsorbent	Parameter of isotherm adsorption						
	Langmuir				Freundlich		
	Xm (mg/g)	K x 10 ⁵ (L/mol)	ΔG (kJ/mol)	R ²	n	K(mol/g) x 10 ¹⁶	R ²
Chitosan	136.09	2.07323	30.53	0.997	0.198	2.39	0.755
Chitosan- p-t-butylcalix[4]arene	147.35	7.23333	33.65	0.998	0.184	25.1	0.600

Dye adsorption isotherm Procion Red MX 8B on chitosan and chitosan-p-t-butylcalix[4]arene tend to followed the model of Langmuir adsorption isotherm, which indicates that both adsorbent occurs at monolayer adsorption. The maximum adsorption happens when all of the active sites of the adsorbent filled by adsorbat forming monolayer. In addition Langmuir models indicated that the adsorption process was chemisorpsi. Comparison of adsorption capacity optimum of adsorbents that have been used to adsorb dye Procion Red MX 8B showed that the adsorbent chitosan and chitosan-p-t-butylcalix[4]arene had a capacity of optimum adsorption was greater than the adsorbent others, as shown in Table 3.

Table 3. Adsorption of dye Procion Red MX 8B by several adsorbent

Adsorbent	qm (mg/g)
PSF-EGDE-CTS [8]	40.69
Pineapple leaf fiber [1]	6.38
Chitosan Sulfate [12]	13.76
Chitosan	136.09
chitosan-p-t-butylcalix[4]arene	147.35

3.4. Adsorbent characterization With FTIR

Characterization adsorbent using an infrared spectrophotometer was performed to identify the functional groups contained in the adsorbent. Results of FTIR spectrum of dye Procion Red MX 8B as well as the combination of chitosan before being used to adsorb dye Procion Red MX 8B and chitosan after being used to adsorb dye Procion Red MX 8B shown in Table 4.

Table 4. Comparison of the functional group of dye Procion Red MX 8B, chitosan before and after adsorbed the dye Procion Red MX 8B

Compound	wavenumber (cm ⁻¹)	functional groups
Dye <i>Procion Red MX 8B</i>	3440.09	Groups of hydroxy (-OH)
	1537.22	Groups of -C=C- aromatic
	1471.64	Groups of N=N azo
	1244.05; 1217.04	Groups of S=O
	752.21	Groups of C-S
	636.49	Groups of C-Cl
Chitosan before adsorbed <i>Procion Red MX 8B</i>	3445.79 ; 3421.72	Groups of hydroxy (-OH) or
		Groups of amine (-NH ₂)
	2872.01	Groups of C-H sp ³
	1575.84	Groups of C=C aromatic
	1419.61; 1463.97	Groups of methylen (-CH ₂ -)
	1029.99	Groups of CN
Chitosan adsorbed <i>Procion Red MX 8B</i>	3383.14	Groups of hydroxy (-OH) atau
		Groups of amine (-NH ₂)
	2956.87	Groups of -Csp ³ -H stretching
	1481.33	Groups of N=N azo
	1201.65 ; 1240.23	Groups of S=O
	742.59	Groups of C-S
	671.23	Groups of C-Cl

The analysis of FTIR Procion Red MX 8B of chitosan-p-t- butylcalix[4]arene before it is used to adsorb and chitosan-p-t- butylcalix[4]arene once used to adsorb dye Procion Red MX 8B shown in Table 5.

Table 5. Comparison of functional groups dye Procion Red MX 8B, the chitosan-p-t-butylcalix[4]arene before and after adsorbed dye Procion Red MX 8B

Compound	wavenumber (cm ⁻¹)	functional groups
Dye Procion Red MX 8B	3440.09 1537.22 1471.64 1244.05; 1217.04 752.21 636.49	Groups of Hydroxy (-OH) Groups of -C=C- aromatic Groups of N=N azo Groups of S=O Groups of C-S Groups of C-Cl
Chitosan-p-t-butylcalix[4]arene before adsorbed Procion Red MX 8B	3419.79 ; 3346.50 3026.31; 3055.24 2868.15 1519.91; 1575.84 1361.74 675.09	Groups of Hydroxy (-OH) or Groups of Amine (-NH ₂) Groups of -CH- aromatic (sp ²) Groups of -CH- sp ³ Groups of C=C aromatic Groups of Methyl (-CH ₃) Groups of C-Cl
Chitosan-p-t-butylcalix[4]arene adsorbed Procion Red MX 8B	3441.01 2949.16; 2929.87 1469.76 1325.10 1201.65.1242.16 702.09 661.58	Groups of Hydroxy (-OH) or Groups of Amine (-NH ₂) Groups of -Csp ³ -H stretching Groups of N=N azo Groups of Methyl (-CH ₃) Groups of S=O Groups of C-S Groups of C-Cl

3.5. Adsorbent characterization By SEM – EDX

Morphology adsorbent chitosan before and after adsorption were characterized using Scanning Electron Microscopy (SEM) as shown in Figure 4.

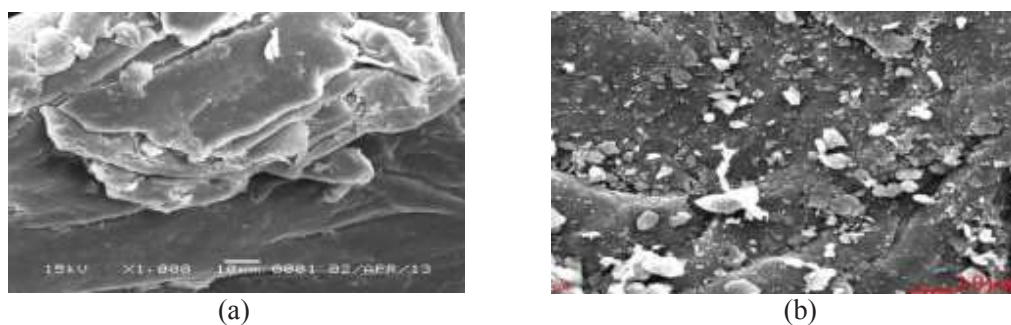


Figure 4. Results SEM of Chitosan before adsorption (a), after adsorption (b)

Figure 4 showed the difference in structure between the adsorbent chitosan before and after adsorbed. Adsorbent chitosan before adsorb dye is shown in Figure 4a, showing slotted structure which allows the adsorbate dye can meet the gap on the surface of chitosan. Chitosan adsorbent to adsorb dye that had been shown in Figure 4b, in which the seen surface structure is already covered by the dye Procion Red MX 8B. Chitosan adsorbent composition was analyzed using SEM-EDX with the results shown in Table 6.

Table 6. Composition of Chitosan adsorbent before and after adsorption

Composition	Chitosan before adsorbed (% mass)	Chitosan after adsorbed (% mass)
C	41.10	62.42
N	22.39	08.13
O	36.51	27.18
Na	-	0.14
S	-	1.11
Cl	-	1.12

While the results of SEM analysis of adsorbent chitosan-p-t-butylcalix[4]arene before and after adsorption was shown in Figure 5.

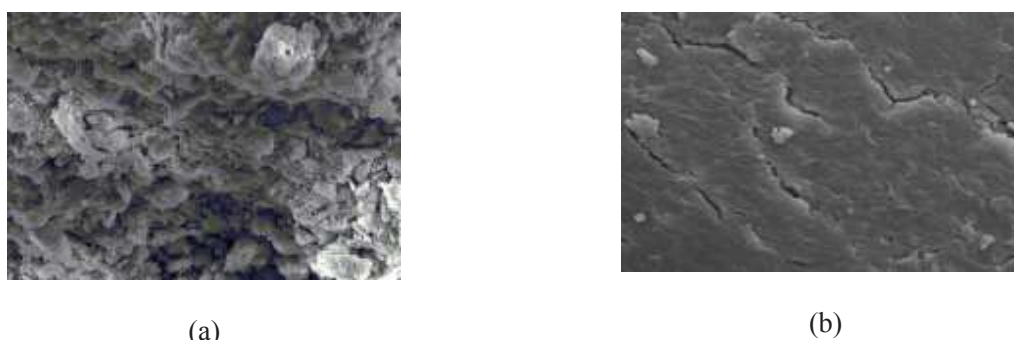


Figure 5. Results SEM of chitosan-p-t-butylcalix[4]arene before adsorption (a), after adsorption (b)

Based on Figure 7 shown the difference in structure between the adsorbent chitosan- p-t-butylcalix[4]arene before and after adsorption. Adsorbent chitosan-p-t-butylcalix[4]arene before adsorption (Figure 5a) shown the structure more porous compared to chitosan, which allows adsorbate dye can meet more porous compared to chitosan. Adsorbent chitosan-p-t-butylcalix[4]arene after adsorption (Figure 5b) shown the structure of the surface has been coated by a dye Procion Red MX 8B. Chitosan adsorbent composition was analyzed using SEM-EDX with the results shown in Table 7.

Table 7. Composition of chitosan- p-t-butylcalix[4]arene adsorbent before and after adsorption

Composition	Chitosan p-t-butylcalix[4]arene before adsorbed (% mass)	Chitosan-p-t-butylcalix[4]arene after adsorbed (% mass)
C	53.95	56.64
N	18.37	10.03
O	7.55	31.62
S	-	1.35
Cl	20.13	0.20
Na	-	0.16

4. Conclusion

Adsorption of dye Procion Red MX 8B using chitosan-p-t-butylcalix[4]arene had a maximum capacity and adsorption energy of 147.35 mg/g and 33.65 KJ/mol, While adsorption kinetics study followed the pseudo second-order kinetics (Ho) with adsorption rate constants for $2.03 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$.

Aknowledgment

The financial support from Indonesian Directorate General of Higher Education through the research project of Penelitian Unggulan Perguruan Tinggi (PUPT) 2015 is greatly appreciated.

References

- [1] Setyoningsih., 2010, *Aplication of fiber Pineapple leaves Adsorbent Dye Procion Red MX 8B*, Thesis, Surakarta: FMIPA Universitas Sebelas Maret.
- [2] Huger K, 2003, *Industrial Dyes: Chemistry, Properties, Applications*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
- [3] Aryunani., 2003, *adsorption of dye Remazol Yellow FG in affluent batik by water hyacinth with NaOH activator*, Thesis, Surakarta: FMIPA Universitas Sebelas Maret.
- [4] Sivaiah M V, Venkatesan, K A, Sasidhar P, Krishna R M, dan Murthy G S, 2004 *J. Nuc.Radiochem. Sci.*, **5**, 1, 7-10.
- [5] Manurung R, 2000, *Recast Azo Reactive Dyes In Anaerobic - Aerobic. e-USU Repository* : Universitas Sumatera Utara.
- [6] Safrianti I, Nelly W, dan Titin A Z, 2012 *JKK*, **1**, 1-7.
- [7] Sardjono R E, 2007, *Synthesis and Aplication of tetramer Cyclical Series calixresorsinarene, alkoxy alkylarene, and Alkenylcalixarene for Adsorption Heavy Metal Cations. Dissertation*. FMIPA, Universitas Gajah Mada, Yogyakarta.
- [8] Kusumaningsih T, Handayani D S, and Lestari Y, 2004 *Alchemy jurnal penelitian kimia*, **8**, 47-56.
- [9] Nur R S, 2007, *Synthesis of pillared clays Cetyltrimethylammonium-Aluminium (CTMA-Al) From Natural Clays and Utilization as Karmina Indigo Dye Adsorbent. In: Seminar Final UNDIP S1 Department of Chemistry, Department of Chemistry, UNDIP*.
- [10] Rouquerol F, J Rouquerol, and K Sing. 1999. *Adsorption by Powders and Porous Solids: Principles, Methodology, and Applications*. San Diego: Academic Press. ISBN 0125989202
- [11] Emma R, M T Suhartono, Dahrul S, and Sugiyono, 2004 *Jurnal Fakultas Perikanan dan Ilmu Kelautan*, Universitas Padjadjaran.
- [12] Astuti P, 2007, *Adsorption of Dyes Textile Waste Procion Red MX 8B By Chitosan and Chitosan Sulfate deacetylation Results Shells Snails (Achatina fullica)*, Thesis, Surakarta: FMIPA Universitas Sebelas Maret.
- [13] Linane P and Shinkai S, 1994, *Calixarenes : Adaptable Hosts Par Excellence*, Chem. Ind., 811 - 814.
- [14] Handayani D S, Purnawan C, Pranoto, Hastuti S, and Hilmiyana D, 2016 IOP Conf. Series: Materials Science and Engineering **107** (2016) 012011 doi:10.1088/1757-899X/107/1/012011
- [15] Handayani D S, Kusumaningsih T and Restuti A, 2014 *Prosiding ICOPIA* part of series: Advance in Physic Research Atlantis Press 21-25
- [16] Izadyar S and Rahimi M, 2007 *Pakistan Journal of Biological Sciences*, **10**, 287-293.
- [17] Sakayawong N, Thiravetyan P, and Nakbanpote W, 2005 *Journal of Colloid and Interface Science*, **286**, 36-42.
- [18] Christie R M, 2001, *Colour Chemistry*, RSC Paperback, The Royal Society of Chemistry, Manchester.